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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of :
Denise Anderson and Georg Fráter

Serial No.: 09/249,384

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Examiner: not yet assigned

Group Art Unit: 1621

For: **ARYL-ACRYLIC ACID ESTERS**

New York, New York
March 15, 1999

TRANSMITTAL OF PRIORITY DOCUMENT

Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

Enclosed please find a certified copy of the following priority document for the above-identified patent application:

1. Application No. 98810114.3, filed on February 13, 1998 in Europe.

Applicants claim priority based on the aforesaid application under the provisions of 35 U.S.C. § 119.

I hereby certify that this correspondence is being deposited with the United States Postal Service as first class mail in an envelope addressed to the Assistant Commissioner for Patents, Washington, D.C. 20231, on March 15, 1999.

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Bescheinigung | Certificate | Attestation

Die angehefteten Unterlagen stimmen mit der ursprünglich eingereichten Fassung der auf dem nächsten Blatt bezeichneten europäischen Patentanmeldung überein.

The attached documents are exact copies of the European patent application described on the following page, as originally filed.

Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet européen spécifiée à la page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

98810114.3

Der Präsident des Europäischen Patentamts:
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
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C. PASTUREL

DEN HAAG, DEN
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Blatt 2 der Bescheinigung
Sheet 2 of the certificate
Page 2 de l'attestation

Anmeldung Nr.:
Application no.: 98810114.3
Demande n°:

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Date of filing: 13/02/98
Date de dépôt:

Anmelder:
Applicant(s):
Demandeur(s):
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Bezeichnung der Erfindung:
Title of the invention:
Titre de l'invention:
Aryl-acrylic acid esters

In Anspruch genommene Priorität(en) / Priority(ies) claimed / Priorité(s) revendiquée(s)

Staat: State: Pays:	Tag: Date: Date:	Aktenzeichen: File no. Numéro de dépôt:

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Remarques:

The present invention relates to 3-(2-substituted aryl)-acrylic acid esters, especially 3-(2-hydroxyaryl)-acrylic acid esters and 3-(2-aminoaryl)-acrylic acid esters. These compounds are useful as precursors for organoleptic compounds, especially for flavours, fragrances and masking agents, antimicrobial compounds and for fluorescent whitening agents.

A principal strategy currently employed in imparting odours to consumer products is the admixing of the fragrance directly into the product. There are, however, several drawbacks to this strategy. The fragrance material can be too volatile and/or too soluble, resulting in fragrance loss during manufacturing, storage, and use. Many fragrance materials are also unstable over time. This again results in loss during storage.

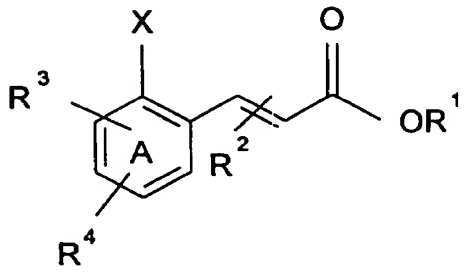
In many consumer products it is desirable for the fragrance to be released slowly over time. Micro-encapsulation and inclusion complexes with cyclodextrins have been used to help decrease volatility, improve stability and provide slow-release properties. However, these methods are for a number of reasons often not successful. In addition, cyclodextrins can be too expensive.

Fragrance precursors for scenting fabrics being washed in the presence of a lipase-containing detergents are described in WO 95/04809. The fragrance precursors contained in the detergent and/or in the softener are cleaved by the lipase and a single active compound, either an odoriferous alcohol or aldehyde or ketone is yielded. Thereby a prolonged scenting effect on the fabric is obtained. The need for a lipase-containing detergent is limiting. In many parts of the world, detergents do not contain lipase. Other consumers prefer to use 'nonbio' detergents.

Fluorescent whitening agents or brighteners have been added to laundry detergents since the 1950s to help maintain the original brightness of white clothing.

One object of the present invention is to provide new precursors for compounds with different activities and thus impart different activities to a product by the addition of just one compound. A further object of the invention is to provide new compounds which are stable under transport and storage conditions. A further object of the present invention is to provide precursor molecules supplying different active compounds simultaneously or successively.

The present invention relates to 3-(2-substituted aryl)-acrylic acid esters of the formula I



wherein

A is a benzene or naphthalene ring,

R^1 is a saturated or unsaturated, straight or branched C_{10}-C_{30} hydrocarbon residue which can contain heteroatoms, can be substituted by an ionic substituent or is the residue of an olfactive alcohol,

R^2 in 1- or 2-position is hydrogen, a straight or branched C_1-C_6 residue; an optionally substituted aromatic or optionally substituted heterocyclic residue,

R^3 and R^4 stand for hydrogen, a straight or branched C_1-C_6 alkyl or C_1-C_6 alkoxy residue, a substituted or condensed heterocyclic residue, -OH, $-NO_2$, $-NH_2$, $-N(C_1\text{-}C_6 \text{ alkyl})_2$, $-N(\text{hydroxyalkyl})_2$, $-NHCO_2CH_3$ or -NH(heterocycle),

R^2, R^3 and R^4 may be the same or different,

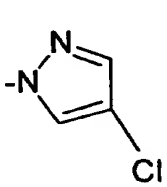
X stands for -OH or NHR^6, wherein R^6 is hydrogen a saturated or unsaturated, straight or branched C_1-C_{20} hydrocarbon or an optionally substituted aromatic or heterocyclic residue,

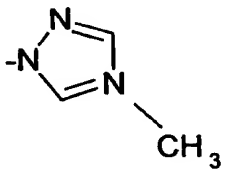
and the acrylic double bond is of the E configuration.

In the above formula I, all possible enantiomers and diastereomers and all mixtures are included within the scope of the invention.

Compounds wherein R^1 is a saturated or unsaturated, straight or branched C_{10}-C_{30} hydrocarbon residue containing one or more O and/or N atoms and/or C(O) groups or substituted by an ionic substituent of the formula $NR^5{}_3{}^+$, in which R^5 is the residue of a fatty acid or an alkyl group with 1 to 30 carbon atoms are preferred.

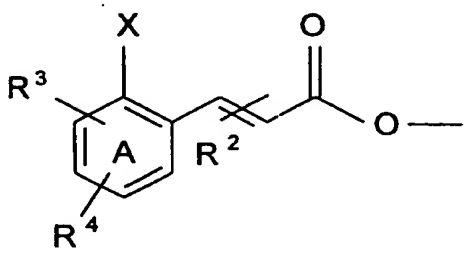
R^2 is preferably a heterocyclic residue of the formula



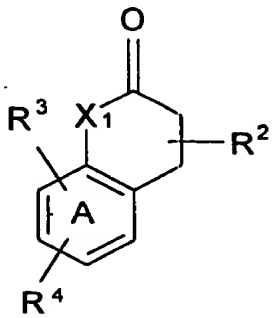


R^3 and/or R^4 are preferably hydrogen, $-N(C_1-C_6$ alkyl$)_2$, $-NH_2$, a five membered heterocyclic residue optionally containing N and/or O atoms, substituted by C_1-C_6 aliphatic and/or aromatic substituents.

The compounds of formula I are mostly or nearly odourless at room temperature, atmospheric conditions and about 20 to 100 % relative humidity. However, under activating conditions, they are cleaved. Thereby the residue of formula Ia



yields a coumarin of the formula II

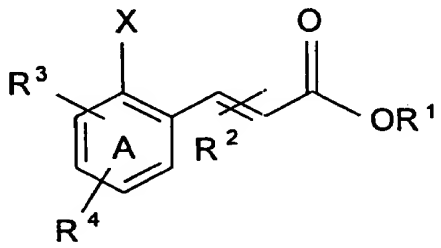


wherein X^1 stands for O or NR^6, R^1, R^2, R^3, R^4 have the meaning as defined above. The coumarins of formula II can

have organoleptic and/or antimicrobial properties and/or optical brightening activity. Preferred are coumarins with olfactive properties. The alcohols possess preferably organoleptic properties. Therefore, upon cleavage two active compounds with the above properties can be obtained. Thus, the compounds of formula I permit the development of useful consumer products with enhanced organoleptic and/or antimicrobial properties and/or optical brightening properties. The organoleptic coumarins and alcohols obtained are useful as fragrances, flavours, masking agents and antimicrobial agents.

The activating conditions which lead to cleavage and thereby to the desired active compounds comprise the presence of UV light such as sunlight and elevated temperatures.

The invention relates also to the use of compounds of formula I



wherein

A is a benzene or naphthalene ring,

R^1 is hydrogen unsaturated or saturated straight or branched C_1-C_{30} hydrocarbon residue which can contain heteroatoms, can be substituted by ionic substituent or is the residue of an olfactive alcohol,

R^2 in 1- or 2-position is hydrogen, a straight or branched C_1-C_6 residue; an aromatic or optionally substituted heterocyclic residue,

R^3 and R^4 stand for hydrogen, a straight or branched C_1-C_6 alkyl or C_1-C_6 alkoxy residue, a substituted or condensed heterocyclic residue, -OH, $-NO_2$, $-NH_2$, $-N(C_1\text{-}C_6 \text{ alkyl})_2$, $-N(\text{hydroxyalkyl})_2$, $-NHCO_2CH_3$ or -NH(heterocycle),

R^2, R^3 and R^4 may be the same or different,

X stands for -OH or NHR^6, wherein R^6 is hydrogen a saturated or unsaturated, straight or branched C_1-C_{20} hydrocarbon or an optionally substituted aromatic or heterocyclic residue,

and the acrylic double bond is of the E configuration,

as precursors for organoleptic compounds, e.g. flavours, fragrances, odour masking agents and as precursors for

antimicrobial agents and as precursors for fluorescent whitening agents.

The esters of formula I can act as fragrance precursors in laundry products. They can also act as precursors for odour masking agents in the same products as the fragrance precursors. They also can act as precursors for antimicrobial agents. In addition, they can also act as precursors for fluorescent whitening agents. The fragrance precursors and the precursors for odour masking agents as well as the flavour precursors of the invention may be used individually in an amount effective to enhance or to mask the characteristic odour or flavour of a material. More commonly, however, the compounds are mixed with other fragrance or flavour components in an amount sufficient to provide the desired odour or flavour characteristics.

The brightener precursors may be used also individually in an effective amount and mixed with one or more other brightener or colorant substance.

Due to the in situ generation of the active compounds the desired effect is prolonged and the substantivity on different substrates is enhanced. If two active compounds are provided by one ester of the formula I, they can be generated, depending on the precursor and/or the activating conditions, simultaneously or successively.

Further, the precursors of the invention provide slow release of the active compounds.

Examples of alcohols R^1OH generated upon cleavage and constituting the residue R^1 in the compounds of formula I are:

amyl alcohol
hexyl alcohol*
2-hexyl alcohol*
heptyl alcohol*
octyl alcohol*
nonyl alcohol*
decyl alcohol*
undecyl alcohol*
lauryl alcohol*
myristic alcohol
3-methyl-but-2-en-1-ol*
3-methyl-1-pentanol
cis-3-hexenol*
cis-4-hexenol*
3,5,5-trimethyl hexanol
3,4,5,6,6-pentamethylheptan-2-ol*
citronellol*
geraniol*
oct-1-en-3-ol
2,5,7-trimethyl octan-3-ol
2-cis-3,7-dimethyl-2,6-octadien-1-ol

6-ethyl-3-methyl-5-octen-1-ol*

3,7-dimethyl-oct-3,6-dienol*

3,7-dimethyloctanol*

7-methoxy-3,7-dimethyl-octan-2-ol*

cis-6-nonenol*

5-ethyl-2-nonanol

6,8-dimethyl-2-nonanol*

2,2,8-trimethyl-7 (8)-nonene-3-ol

nona-2,6-dien-1-ol

4-methyl-3-decen-5-ol*

dec-9-en-1-ol

benzylalcohol

2-methyl undecanol

10-undecen-1-ol

1-phenyl ethanol*

2-phenyl ethanol*

2-methyl-3-phenyl-3-propenol

2-phenyl propanol*

3-phenyl propanol*

4-phenyl-2-butanol

2-methyl-5-phenyl pentanol*

2-methyl-4-phenyl-pentanol*

3-methyl-5-phenyl-pentanol*

2-(2-methylphenyl)-ethanol*

4-(1-methylethyl)benzene methanol

4-(4-hydroxyphenyl)butan-2-one*

2-phenoxy ethanol*

4-(1-methylethyl)-2-hydroxy-1-methyl benzene

2-methoxy-4-methyl phenol

4-methyl phenol

anisic alcohol*

p-tolyl alcohol*

cinnamic alcohol*

vanillin*

ethyl vanillin*

eugenol*

isoeugenol*

thymol

anethol*

decahydro 2-naphthalenol

borneol*

cedrenol*

farnesol*

fenchyl alcohol*

menthol*

3,7,11-trimethyl-2,6,10-dodecatrien-1-ol

alpha ionol*

tetrahydro ionol*

2-(1,1-dimethylethyl)cyclohexanol*

3-(1,1-dimethylethyl)cyclohexanol*

4-(1,1-dimethylethyl)cyclohexanol*

4-isopropyl cyclohexanol

6,6-dimethyl-bicyclo [3.3.1]hept-2-ene-2-ethanol

6,6-dimethyl-bicyclo [3.1.1]hept-2-ene-methanol*

p-menth-8-en-3-ol*

3,3,5-trimethyl cyclohexanol

2,4,6-trimethyl-3-cyclohexenyl-methanol*

4-(1-methylethyl)cyclohexyl-methanol*

4-(1,1-dimethylethyl)cyclohexanol

2-(1,1-dimethylethyl)-cyclohexanol

2,2,6-trimethyl-alpha-propyl cyclohexane propanol*

5-(2,2,3-trimethyl-3-cyclopentenyl)-3-methylpentan-2-ol*

3-methyl-5-(2,2,3-trimethylcyclopentyl-3-enyl)pent-4-en-2-ol*

2-ethyl-4(2,2,3-trimethylcyclopentyl-3-enyl)but-2-en-1-ol*

4-(5,5,6-trimethylbicyclo[2.2.1] hept-2-yl)-cyclohexanol*

2-(2-methylpropyl)-4-hydroxy-4-methyl-tetrahydropyran*

2-cyclohexyl propanol*

2-(1,1-dimethylethyl)-4-methyl cyclohexanol*

1-(2-tert-butyl-cyclohexyloxy)-2-butanol*

1-(4-isopropyl-cyclohexyl)-ethanol*

2,6-dimethyl-oct-7-en-2-ol**

2,6-dimethyl-heptan-2-ol**

3,7-dimethyl-octa-1,6-dien-3-ol**

whereby * indicates the preferred alcohols and ** indicate the more preferred alcohols.

Examples of fluorescent whitening coumarins of formula II generated upon cleavage and constituting the respective residue in the compounds of formula I are:

7-(3-methyl-1H-pyrazol-1-yl)-3-phenyl-2H-1-benzopyran-2-one

7-(4-methyl-5-phenyl-2H-1,2,3-triazol-2-yl)-3-phenyl-2H-1-benzopyran-2-one

7-(2H-naphtho[1,2-d]triazol-2-yl)-3-phenyl-2H-1-benzopyran-2-one

3-(1H-pyrazol-1-yl)-7-(2H-1,2,3-triazol-2-yl)-2H-1-benzopyran-2-one

7-(dimethylamino)-1-methyl-3-phenyl-2(1H)-quinolinone

7-(diethylamino)-1-ethyl-3-phenyl-2(1H)-quinolinone

7-amino-4-methyl-2H-1-benzopyran-2-one

7-(dimethylamino)-4-methyl-2H-1-benzopyran-2-one

7-(diethylamino)-4-methyl-2H-1-benzopyran-2-one

7-hydroxy-4-methyl-2H-1-benzopyran-2-one

6,7-dihydroxy-2H-1-benzopyran-2-one

Examples for coumarins of formula II with olfactive properties generated upon cleavage and constituting the respective residue in the compounds of formula I are:

2H-1-benzopyran

3-methyl-benzopyran-2-one

8-(1,1-dimethylethyl)-6-methyl-benzopyrone

4-methyl-7-ethoxy-coumarin

6-methyl-2H-1-benzopyran

It is a matter of course, that it is not possible to give a complete list of the active coumarins and alcohols which are generated as a result of the desired cleavage of the acrylic acid esters of formula I by UV-light and/or by

elevated temperatures. The skilled person is, however, quite aware of those alcohols and coumarins which provide the desired organoleptic, e.g. fragrance, flavour and odour masking, antimicrobial and/or brightening effects.

The compounds of formula I may preferably be used sustained release odorants and flavours but also as sustained agents to mask or attenuate undesirable odours or to provide additional odours not initially present in consumer products, i.e. laundry detergents, fabric softeners, fabric softener sheets, toiletries and cosmetics such as sunscreens. Further applications are sustained brighteners and antimicrobial agents in the same products. The brighteners are especially useful for wool, rayon and polyamides. These compounds are also useful for flavouring and aromatizing tobacco products, e.g. cigarettes.

The amount required to produce the desired, overall effect varies depending upon the particular compounds of formula I chosen, the product in which it will be used, and the particular effect desired.

For example, depending upon the selection and concentration of the compound chosen, when a compound of the formula I is added either singly or as a mixture, e.g. to a laundry product composition at levels ranging from about 0.001 to about 10 % by weight, a coumarin and if

desired an odoriferous alcohol in an organoleptically effective amount is released when the product is used. These newly formed odorant(s) serve to enhance the odour of the fragrance. Depending on the compound of formula I an antimicrobial agent or a brightener can be released.

Depending upon the selection and concentration, addition of the compounds I, either singly or as a mixture, to cigarette tobacco at levels ranging from about 5 ppm to about 50'000 ppm tends to enhance the smoking flavour and/or mask undesirable smoking odours. An important property of these compounds I is that the flavourant or odorant is covalently bound as a non-volatile compound and the flavourant or odorant is released only when the tobacco product is ignited and burns.

Addition of the compounds of formula I either separately or as a mixture at levels suitably ranging from about 5 ppm to about 50'000 ppm by weight onto the media enclosing the tobacco serves to incorporate the odorant/flavourant in the side-stream smoke of the tobacco. Air borne flavourants and/or odorants are thus introduced. This newly formed odorant or flavourant serves to enhance or mask the smoking odours depending upon selection and use levels of the compounds I.

As is evident from the above compilation of alcohols and coumarins, a broad range of known odorants or flavours or

mixtures can be generated from precursors of the invention. While manufacturing compositions the precursors of the invention may be used according to methods known to the perfumer, such as e.g. from W.A. Poucher, Perfumes, Cosmetics, Soaps, 2, 7th Edition, Chapman and Hall, London 1974. The fluorescent whitening agents may be added in the same manner.

The compounds of formula I can be prepared by using standard methods known to the skilled chemist. Convenient methods are outlined in the Examples without limiting the invention thereto.

Example 1

(E)-3-(2-Hydroxy-phenyl)-2-methyl-acrylic acid ethyl ester

To a solution of 75.0 g (carbethoxyethylidene)triphenyl phosphorane in 350 ml of toluene, 23.2 g of salicylaldehyde was dropped in at 20°C while cooling in an ice-bath. After stirring at room temperature for 90 min., the reaction mixture was diluted with toluene and washed to neutrality with water. The organic phase was dried, filtered and evaporated to dryness. The resulting yellow oil was purified by chromatography to yield 35.5 g of a colourless solid.

NMR ($CDCl_3$) δ 7.82 (s, 1H), 7.30-6.85 (m, 4H), 6.6 (s, OH), 4.35-4.17 (q, 2H), 2.04 (s, 3H), 1.40-1.28 (t, 3H)

Example 2

(E)-3-(2-Hydroxy-phenyl)-acrylic acid methyl ester

According to the procedure of Example 1, (E)-3-(2-hydroxy-phenyl)-2-methyl-acrylic acid methyl ester was prepared from methyl(triphenyl-phosphoranylidene)acetate and salicylaldehyde.

Example 3

(E)-3-(2-Hydroxy-phenyl)-acrylic acid ethyl ester

According to the procedure of Example 1, (E)-3-(2-hydroxy-phenyl)-2-methyl-acrylic acid methyl ester was prepared from ethyl(triphenyl-phosphoranylidene)acetate and salicylaldehyde.

Example 4

(E)-3-(2-Hydroxy-phenyl)-2-methyl-acrylic acid

To a solution of 35.5 g of (E)-3-(2-hydroxy-phenyl)-2-methyl-acrylic acid ethyl ester in 600 ml of ethanol, a

solution of 10.66 g of potassium hydroxide in 500 ml of water was dropped in. After refluxing for 5 hours, another 5.0 g of potassium hydroxide was put in and the mixture was refluxed for another 19 hours. Then the reaction mixture was cooled down, diluted with ether and washed to pH 4 with HCl 2N and water. The organic phase was dried, filtered and evaporated to dryness. The resulting colourless crystals were not further purified.

NMR ($CDCl_3$) δ 7.90 (s, 1H), 7.31-6.83 (m, 4H), 2.07 (s, 3H)

Example 5

(E)-3-(2-Hydroxy-phenyl)-2-methyl-acrylic acid 3,7 dimethyl-oct-6-enyl ester

A solution of 6.0 g of (E)-3-(2-hydroxy-phenyl)-2-methyl-acrylic acid, 5.3 g of citronellol and 1g of p-toluene-sulfonic acid in 150 ml of cyclohexane was refluxed for 6.5 hours using a water separator. Then the reaction mixture was cooled down, diluted with hexane and washed to neutrality with saturated sodium bicarbonate and water. The organic phase was dried, filtered and evaporated to dryness. The resulting yellow oil was purified by chromatography to yield 6.45 g of a colourless oil.

NMR ($CDCl_3$) δ 7.80 (s, 1H), 7.38-6.83 (m, 4H), 6.4 (s, OH), 5.09 (t, 1H) 4.25 (t, 2H), 2.10-1.90 (m, 5H), 1.88-1.08 (m, 11H), 0.93 (d, 3H)

Example 6

(E)-3-(2-Hydroxy-phenyl)-2-methyl-acrylic acid phenethyl ester

According to the same procedure of Example 3, (E)-3-(2-hydroxy-phenyl)-2-methyl-acrylic acid phenethyl ester was prepared from 3-(2-hydroxy-phenyl)-2-methyl-acrylic acid, phenyl ethyl alcohol and p-toluenesulfonic acid.

Example 7

3-(4-Diethylamino-2-hydroxy-phenyl)-but-2-enoic acid ethyl ester

To a suspension of 5.27 g ethoxycarbonylmethylene-triphenylphosphorane in 10 ml of toluene, a solution of 2.02 g 1-(4-diethylamino-2-hydroxy-phenyl)-ethanone (DE 28 44 606) was dropped in at room temperature. Then the reaction mixture was heated to reflux. After refluxing for 31 hours the mixture was cooled down and evaporated to dryness. The resulting dark oil was purified by chromatography to yield a colourless oil.

NMR ($CDCl_3$) δ 7.22-7.09 (m, 1H), 6.57-6.42 (m, 1H), 6.32-6.20 (m, 2H), 5.01 (s, 1H), 4.18-4.01 (q, 2H), 3.42-3.24 (q, 4H), 2.49 (s, 3H), 1.31-1.08 (m, 9H).

The compounds of Examples 1-4 yield upon cleavage organoleptic coumarins, Examples 5 and 6 organoleptic coumarins and organoleptic alcohols and Example 7 a brightener coumarin.

Example 8

(E)-3-(2-Hydroxy-5-methylphenyl)-acrylic acid ethyl ester

(E)-3-(2-Hydroxy-phenyl)-acrylic acid ethyl ester was prepared according to the procedure of Bunce and Moore, Org. Prep. Proc. 29(3), 293, (1997).

Example 9

Test cloth was washed with detergent to which one or more of the precursors of Examples 1-6 had been added. The cloth was then line dried. The cloth dried in sunlight had a distinct coumarin note, as determined by a trained panel. In contrast, the cloth dried without sunlight was olfactively neutral.

Example 10

Test cloth was washed with a detergent and then a fabric softener, containing one ore more of the precursors of Examples 1-6 was added to the rinse cycle. The cloth was then line dried. The cloth dried in sunlight had a distinct coumarin note, as determined by a trained panel. In contrast, the cloth dried without sunlight was olfactively neutral.

Example 11

A 1% solution of one or more of the products of Examples 1-6 in ethanol was applied to cigarette papers to produce levels of 5-50'000 ppm of each flavourant. The paper was incorporated in cigarettes and, upon burning, released a fragrant odour.

Example 12

A broad spectrum (UV-A and UV-B) oil/water sunscreen lotion was prepared with 0,5%.

Part A

Recipe:%	Compound	Chemical Name
2 %	PARSOL MCX	Octyl methoxycinnamate
3 %	PARSOL 1789	4-4-Butyl-4'methoxy-

		dibenzoyl methane
12 %	Cétiol LC	Coco-caprylate/caprate
4 %	Dermol 185	Isostearyl neopentanoate
0,25 %	Diethyl-eneglycol monostearate	PEG-2-stearate
1 %	Cetylalcohol	Cetylalcohol
0,25 %	MPOB/PPOB	Methyl-propylparabene
0,1 %	EDTA BD	EDTA-sodium salt
1 %	Amphisol DEA (Giv.)	Diethanolamine cetyl-phosphate

Part B

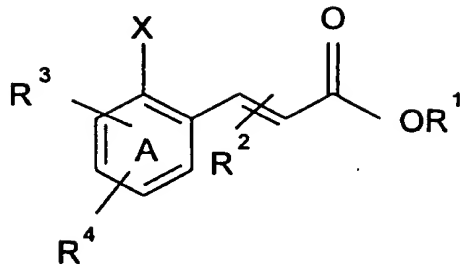
20 %	Permulene TR-1 (+%)	Acrylate C10-C30 Alkyl-acrylate
50,1 %	water deion	water deion
5 %	Propyleneglycol	1,2-Propanediol
0,8 %	KOH (10%)	Potassium hydroxide

Part A was heated in a reactor to 85°C.

Part B was slowly added within 10 min., followed by addition of KOH and 0.5% of the product of Example 5. The emulsion was then cooled and degassed.

Claims

1. Compounds of the formula I



wherein

A is a benzene or naphthalene ring,

R^1 is a saturated or unsaturated, straight or branched C_{10}-C_{30} hydrocarbon residue which can contain heteroatoms, can be substituted by an ionic substituent or is the residue of an olfactive alcohol,

R^2 in 1- or 2-position is hydrogen, a straight or branched C_1-C_6 residue; an optionally substituted aromatic or optionally substituted heterocyclic residue,

R^3 and R^4 stand for hydrogen, a straight or branched C_1-C_6 alkyl or C_1-C_6 alkoxy residue, a substituted or

condensed heterocyclic residue, -OH, $-NO_2$, $-NH_2$, $-N(C_1-C_6$ alkyl$)_2$, $-N$(hydroxyalkyl$)_2$, $-NHCO_2CH_3$ or -NH (heterocycle),

R^2, R^3 and R^4 may be the same or different,

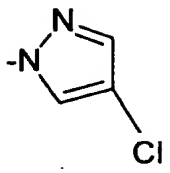
X stands for -OH or NHR^6, wherein R^6 is hydrogen a saturated or unsaturated, straight or branched C_1-C_{20} hydrocarbon or an optionally substituted aromatic or heterocyclic residue,

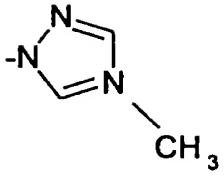
and the acrylic double bond is of the E configuration.

2. Compounds according to claim 1, wherein R^1 is a saturated or unsaturated, straight or branched $C_{10}-C_{30}$ hydrocarbon residue containing one or more O and/or N atoms and/or C(O) groups.

3. Compounds according to claim 1, wherein R^1 is a saturated or unsaturated, straight or branched $C_{10}-C_{30}$ hydrocarbon residue substituted by an ionic substituent of the formula $NR^5{}_3{}^+$, in which R^5 is the residue of a fatty acid or an alkyl group with 1 to 30 carbon atoms.

4. Compounds according to one of the preceding claims, wherein R^2 is a heterocyclic residue of the formula





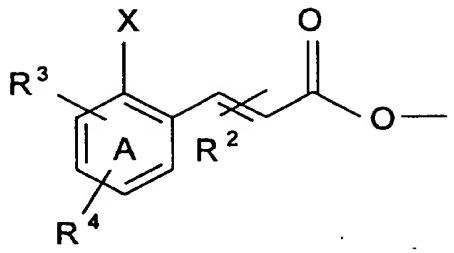
5. Compounds according to one of the preceding claims, wherein R^3 and/or R^4 are five membered heterocyclic residues containing N and/or O atoms.

6. Compounds according to one of the preceding claims, wherein R^3 and/or R^4 is hydrogen, $-N(C_1-C_6$ alkyl$)_2$, $-NH_2$, a five membered heterocyclic residue, substituted by C_1-C_6 aliphatic and/or aromatic substituents.

7. Compounds according to one of the preceding claims, wherein R^2 is hydrogen or methyl.

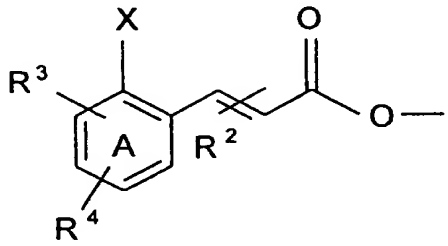
8. Compounds according to one of the preceding claims, wherein R^1 is the residue of an olfactive alcohol.

9. Compounds according to one of the preceding claims, wherein the residue of formula Ia



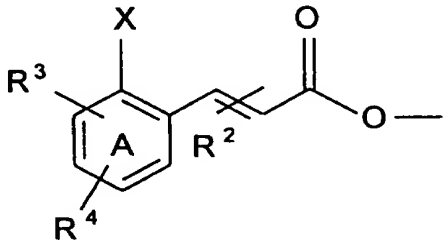
is the precursor for fragrant coumarins.

10. Compounds according to one of the claims 1-8, wherein the residue of formula Ia



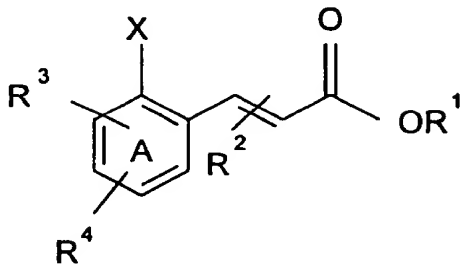
is the precursor for fluorescent whitening coumarins.

11. Compounds according to claims 8 and 9, wherein R^1 is the residue of an olfactive alcohol and the residue of formula Ia



is the precursor for a fragrant coumarin.

12. Use of compounds of formula I



wherein

A is a benzene or naphthalene ring,

R^1 is hydrogen, unsaturated or saturated straight or branched C_1-C_{30} hydrocarbon, can contain heteroatoms, can be substituted by ionic substituent or is the residue of an olfactive alcohol,

R^2 in 1- or 2-position is hydrogen, a straight or branched C_1-C_6 residue; an optionally substituted aromatic or optionally substituted heterocyclic residue,

R^3 and R^4 stand for hydrogen, a straight or branched C_1-C_6 alkyl or C_1-C_6 alkoxy residue, a substituted or

condensed heterocyclic residue, -OH, $-NO_2$, $-NH_2$, $-N(C_1-C_6$ alkyl$)_2$, $-N$(hydroxyalkyl$)_2$, $-NHCO_2CH_3$ or -NH (heterocycle),

R^2, R^3 and R^4 may be the same or different,

X stands for -OH or NHR^6, wherein R^6 is hydrogen a saturated or unsaturated, straight or branched C_1-C_{20} hydrocarbon or an optionally substituted aromatic or heterocyclic residue,

and the acrylic double bond is of the E configuration,

as precursors for organoleptic, antimicrobial compounds and/or fluorescent whitening agents.

13. Use according to claim 12 in laundry products.

14. Use according to claim 12 in tobacco products.

15. Use according to claim 12 in cosmetics and toiletries.

Abstract

The acrylic acid esters of formula I are useful for the delivery of organoleptic compounds, especially for flavours, fragrances and masking agents and antimicrobial compounds. They can also deliver fluorescent whitening agents.